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Hot bands in overtone absorption transitions: High temperature spectra

by

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Center for Photochemical Sciences  
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## Hot Bands In Overtone Absorption Transitions: High Temperature Photoacoustic Spectra

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### Abstract

The laser photoacoustic spectra of the  $4\nu_{\text{N-H}}$  and  $4\nu_{\text{C-H}}$  overtones of pyrrole, the  $5\nu_{\text{C-H}}$  of methyl isocyanide and acetonitrile, the  $5\nu_{\text{C-H}}$  and  $6\nu_{\text{C-H}}$  of isobutane, and the  $6\nu_{\text{C-H}}$  of cyclohexane were measured at temperatures up to 140 C ( $T_{140}$ ) and compared to the room temperature ( $T_R$ ) spectra. Hot bands were identified by their temperature dependence in pyrrole, methyl isocyanide and isobutane. From the change in the relative intensities of the hot band to the main band going from  $T_R$  to  $T_{140}$ , the wavenumbers of the thermally populated states were  $405 \pm 80$ ,  $410 \pm 80$  and  $208 \pm 40 \text{ cm}^{-1}$  for pyrrole, isobutane and methyl isocyanide, respectively. These values compare well to the bending motion frequencies in these molecules.

Large red shifts of the hot bands from the main peak were observed, as expected for high overtone transitions due to large anharmonicities. The anharmonic constants determined from these shifts are  $-25 \text{ cm}^{-1}$  for the N-H in pyrrole and  $-20 \text{ cm}^{-1}$  for the C-H in methyl isocyanide and isobutane. In the case of the N-H absorption the hot band was completely separated from the main transition. In the C-H overtone spectra these hot band absorptions were not separated and result in an apparent increased width of the overtone transition.

### Introduction

The contribution of homogeneous and inhomogeneous broadening in vibrational overtone spectra is still of great experimental and theoretical interest. Based on the local mode theory<sup>1</sup> the high frequency overtones of the C-H stretches in polyatomic molecules are largely uncoupled to the rest of the vibrational modes of the molecule so that structured bands are expected for these transitions<sup>2</sup>. However, most of the observed overtone contours are broader ( $\sim 200 \text{ cm}^{-1}$ ) and less structured than expected. Rotational and vibrational congestion, which leads to inhomogeneous broadening, arises from transitions out of excited rotational and vibrational states which are thermally populated. An absorption which originates from a thermally populated low lying vibrational level is called a hot band. Homogeneous broadening derives from the lifetime of the state and is not temperature dependent. For vibrational overtone levels the lifetime is governed by coupling of the bright state to nearly isoenergetic states which distribute the oscillator strength between them. This broadening reports on intramolecular vibrational relaxation (IVR) and is critical in the search for mode selective chemistry<sup>3</sup>.

In the last 20 years, theoretical and experimental<sup>4-20</sup> studies have investigated homogeneous and inhomogeneous broadening in overtone spectra. The usual procedure for differentiating between homogeneous and inhomogeneous broadening is to record the spectra of cooled samples. At low temperature the number of the thermally populated states and their contribution to the bandwidth is reduced, i.e. the inhomogeneous contribution is decreased. Hydrocarbons can be moderately cooled while maintaining high enough vapor pressure to be detected using photoacoustic spectroscopic methods. Methane and trideuteromethane<sup>21</sup> and several small to medium-size hydrocarbons<sup>22</sup> have been studied using photoacoustic detection. Scherer et al.<sup>21</sup> measured the fifth C-H stretch overtone of methane and CD<sub>3</sub>H at 77K. The spectrum shows a significant reduction in congestion at the low temperature. Crofton et al.<sup>22</sup> measured different C-H stretch overtone spectra of molecules ranging in size from methane to isobutane at 143K or 189 K and compared these to the room temperature contours. Overall the contours were temperature invariant indicating that the homogeneous linewidths were wide relative to the level spacing. The temperature independence correlated loosely with the density of states and the degree of saturation. This effect has been documented many times and now studies are underway to determine by direct measurement the density of states and the dark states which produce the line broadening<sup>23-25</sup>. These studies necessarily begin at lower energies of excitation and involve cooling by supersonic expansion in order to make any progress. For some compounds supersonic expansion dramatically reduces the congestion in the spectra. Reilly and co-workers observed the  $\Delta\nu=4$  of the O-H stretch in water<sup>26</sup> and hydrogen peroxide<sup>27</sup> under jet-cooled conditions using an optothermal bolometric detection method. The spectral linewidths of the overtone transitions are found to be Doppler limited at a few MHz. However, in the same experiment they were not able to detect the  $\Delta\nu=4$  of the N-H stretch in pyrrole<sup>28</sup>, which was explained by substantial vibrational state mixing which increased the homogeneous linewidth. Crim and co-workers studied the overtone spectra of jet-cooled hydrogen peroxide and tetramethyl dioxetane by observing the unimolecular decomposition products<sup>29-30</sup>. While a dramatic reduction in the bandwidths of the vibrational overtone transitions was observed in H<sub>2</sub>O<sub>2</sub>, minor changes observed in the case of tetramethyl dioxetane, suggesting large homogeneous contributions to the bandwidth in the later case. Page et al.<sup>31</sup>, employed supersonic jet cooling with multiphoton ionization (MPI) double-resonance detection to obtain the C-H fundamental, and first and second overtone spectra in benzene. The second overtone of benzene was reinvestigated by Bassi and co-workers<sup>32</sup> under supersonic cooling and optothermal detection. Both of these experiments with benzene show dramatic reduction of the overtone bandwidth at the low temperature of the beam. The large inhomogeneous contributions to the bandwidth in the overtone transitions of benzene will be discussed later.

Indirect evidence for inhomogeneous contribution to the overtone bandwidth was shown in 1,3,5-hexatriene and allyl isocyanide<sup>33-34</sup>. The nonmonotonic dependence of the isomerization rate with energy in these overtone photoisomerization experiments was attributed to the contribution of hot bands.

The above experiments indicate that since the homogeneous linewidth is large, extreme cooling is required to "open up" the spectrum. Unfortunately doing this reduces the vapor pressure of the

sample and the signal will be small beyond the experimental detection limits of photoacoustic spectroscopy. On the other hand if the sample is heated, vibrational hot band absorptions will grow in intensity relative to the other features in the spectrum without sacrificing photoacoustic signal. We have chosen this strategy in looking for vibrational hot bands, heating our samples as high as 140 C. The high temperature is limited by the sensitivity of the microphone used to detect the signal, as described in the experimental section. In addition we watch for band contour shape changes on the outside chance that there may be some effects.

There is some precedence in this arena. The  $3\nu_{\text{N-H}}$  overtone absorption of pyrrole vapor was photographed at 150 and 250 C by Zumwalt and Badger<sup>35</sup>. At the high temperatures the band at  $10111\text{ cm}^{-1}$  (989 nm) increased in intensity relative to the main peak at  $10185\text{ cm}^{-1}$  (981.8 nm). The authors concluded that the peak at  $10111\text{ cm}^{-1}$  was the first member of a sequence deriving from a low frequency vibration populated at the high temperature i.e. a hot band. A large shift of  $74\text{ cm}^{-1}$  of the hot band to the red of the main peak was observed, indicating a large interaction between the N-H stretch and the low frequency mode.

High temperature spectra of the  $5\nu_{\text{O-H}}$  overtone in gaseous ethanol was studied by Fang et al.<sup>36</sup> using photoacoustic absorption spectroscopy. Increasing the temperature from room temperature to 80 C changed the relative intensity of the two peaks belonging to the two conformers in ethanol: trans or gauche configuration of the O-H bond and methyl group. From this temperature dependence the enthalpy difference between the two conformers was determined.

Vibrational hot bands derive their intensity from the main allowed transition and are observed to the red of the principal band due to anharmonicity. Their relative intensity depends on the temperature and the frequency of the low lying level which is thermally populated. The relative intensity expression is simply the Boltzmann description for the population of the level at a particular temperature. Anharmonicities for hot bands observed in the infrared are typically less than a few wavenumbers. These values reflect the harmonic nature of the vibrational potential even when this type of coupling is observed. The spectral shift of the hot band depends on the vibrational quantum numbers which in the infrared are always low values. Vibrational overtone spectra are characterized by local mode absorptions with large anharmonicities. Consequently, the hot band spectral shifts should be large in these absorptions. Baylor et al.<sup>37</sup> observed hot band transitions ( $\nu_9 \rightarrow \nu_9 + \nu\nu_1$ ) accompanying the first to the fifth acetylenic C-H stretch overtone transitions in propyne, where  $\nu_9$  is the  $\text{C}\equiv\text{C-H}$  bending mode. The anharmonic constant obtained from the spectra was  $-23\pm 7\text{ cm}^{-1}$ .

In the present paper, we examined the  $4\nu_{\text{N-H}}$  and  $4\nu_{\text{C-H}}$  overtones of pyrrole,  $5\nu_{\text{C-H}}$  of methyl isocyanide and acetonitrile and the  $5\nu_{\text{C-H}}$  and  $6\nu_{\text{C-H}}$  of isobutane at  $T_{120}$  or  $T_{140}$  and compared these spectra to those at  $T_{\text{rt}}$ . Hot bands were identified in the case of pyrrole, methyl isocyanide and isobutane. In light of our results, we reexamined the second overtone of benzene<sup>31-32</sup> and the  $4\nu_{\text{C-H}}$  (acetylenic) and  $5\nu_{\text{C-H}}$  (methyl) overtones in propyne<sup>22</sup> which have been reported by previous workers.

## Experimental

The overtone absorption spectra were recorded using intracavity photoacoustic techniques as was described previously<sup>38</sup>. A Pyrex cell, 20 cm long and 1.3 cm I.D., outfitted with quartz windows oriented at Brewster's angle, and a microphone (Knowles BT-1751) at the center, was aligned inside the cavity of a Spectra-Physics argon ion pumped dye laser. The microphone signal was directed to a lock-in amplifier (EG&G PAR model 5207) which was modulated at 250 Hz. The modulation frequency was provided by a mechanical chopper (PTI Inc. model 03-0C4000) which chopped the argon laser beam. A motor-driven three plate birefringent filter tuned the dye laser with 3 cm<sup>-1</sup> resolution. The absorption wavelengths were measured with a Spex 1401 double monochromator with resolution of 1 cm<sup>-1</sup>. Both the motor control unit (Oriel model 18007) and the lock-in amplifier were interfaced and controlled with IBM PC computer.

The high temperature spectra were recorded by placing the photoacoustic cell inside an intracavity oven. Two main problems arise in high temperature photoacoustic experiments. First, the microphone sensitivity decreases with increasing temperature, and second, the laser power decreases with heating inside the cavity. Under our experimental conditions, temperatures higher than 140 C were not accessible.

The extracavity power was measured for ratioing the spectra. The shape of the gain curve did not change with temperature, however the overall intensity did decrease. The ratio allows direct comparison of the relative intensity of the peaks in two spectra recorded at different temperatures.

The normal vapor pressure of pyrrole (6-8 torr), methyl isocyanide (~100 torr), acetonitrile (~70 torr) and 100 torr of isobutane were introduced to the photoacoustic cell, and the total pressure in the cell was raised to 200 torr by adding argon. Pyrrole (98%) and acetonitrile (99.9%) were obtained from Aldrich Chemical Co. Methyl isocyanide was synthesized by dehydration of N-methyl formamide method<sup>39</sup>, and isobutane (99.5%) was obtained from Matheson Gas Products. Pyrrole and methyl isocyanide were freshly distilled before use while acetonitrile and isobutane were used without further purification.

## Results

Figures 1 through 9 show comparison of the high and low temperature spectra for the C-H and N-H stretches. Depending on the strength of each overtone transition, the best high temperature signal to noise was obtained at either T<sub>140</sub> or T<sub>120</sub>. The signal intensity decreased at the high temperatures because of the decrease in microphone sensitivity.

As mentioned in the introduction, the relative intensity of the hot bands depends on the temperature and the energy of the low lying level which is thermally populated. The relative intensity expression is simply the Boltzmann description for the population of the level at a particular temperature

$$N_v = C N \exp (- \Delta E / kT) \quad (1)$$

where  $N_v$  is the population of the low energy state,  $C$  is a constant,  $N$  is the population of the ground state,  $\Delta E$  is the energy above the ground state and  $T$  is the temperature. The  $\Delta E$  values can be obtained by comparing the relative intensities of the hot band (h) to the principal band (p) at two temperatures according to the relation

$$N_h(T_1) / N_h(T_2) = N_p(T_1) / N_p(T_2) \exp[ -\Delta E/k (1/T_1 - 1/T_2)] \quad (2)$$

To quantify the relative change in intensity with increasing temperature, we used two different methods. For pyrrole and propyne, where the hot band and principal peak are completely separated, we cut and weighed the two peaks. For the other cases where the peaks overlap, a deconvolution routine was used along with a simple comparison of the peak heights. Although the bandwidths in our spectra are not homogeneous we have used a Lorentzian lineshape for the deconvolution. This was done simply for convenience but the band contours do match our observed spectra quite well in most cases. The Lorentzian band contour formula

$$I(\omega) = k_p \gamma_p / [(\omega - \omega_p)^2 + \gamma_p^2/4] + k_h \gamma_h / [(\omega - \omega_h)^2 + \gamma_h^2/4] \quad (3)$$

has two intensity factors,  $k_p$  and  $k_h$ , the bandwidths,  $\gamma_p$  and  $\gamma_h$ , and  $\omega_p$  and  $\omega_h$  as the peak transition wavenumbers. These values of  $\gamma$  are not related to the homogeneous bandwidth. The values of the relative intensities and the experimental bandwidths (FWHM) are tabulated in Table 1.

The vibrational transition energy is given by<sup>40</sup>

$$\Delta G_0 = G_0(v_1', v_2' \dots) - G_0(v_1, v_2 \dots) \quad (4)$$

where the primed quantum numbers are those of the upper state,  $G_0$  is the vibrational term value referenced to the zero point energy level and expressed as

$$G_0(v_1, v_2 \dots) = \sum \omega_i^0 v_i + \sum \sum x_{ik} v_i v_k \quad (5)$$

where  $v_i$  and  $v_k$  are the vibrational quantum numbers,  $\omega_i^0$  are the frequencies and the  $x_{ik}$ 's are the anharmonicities for coupling between the  $i^{\text{th}}$  and  $k^{\text{th}}$  vibrational modes. For vibrational overtone transitions, where the local mode picture best describes the appearance of the spectrum, the principal peak transition in wavenumbers can be obtained from equation 4 assuming all the other quantum numbers are zero, as follows

$$\Delta G_0^p = G_0(v_p, 0) - G_0(0, 0) = v_p \omega_p^0 + x_{pp}^0 v_p^2 \quad (6)$$

and the hot band transition as

$$\Delta G_0^h = G_0(v_p, v_h) - G_0(0, v_h) = v_p \omega_p^0 + x_{pp}^0 v_p^2 + x_{ph}^0 v_p v_h \quad (7)$$

From equations 6 and 7, the spectral shift of the hot band can be obtained as

$$\Delta G_0^p - \Delta G_0^h = x_{ph}^0 v_p v_h \quad (8)$$

Equation 8 shows that the spectral shift of the hot band depends directly on the vibrational quantum numbers. Taking  $v_h=1$  and  $v_p=4, 5$  or  $6$  depending on the specific overtone, the anharmonic constants  $x_{ph}^0$  were obtained from the measured spectral shifts and tabulated in Table 1. Our observed large spectral shifts of the hot bands are consistent with the large quantum numbers in the overtone transitions in addition to the large anharmonicities which characterize local mode absorptions.

## Discussion

### Pyrrole

The complete vibrational overtone spectrum of pyrrole is known<sup>38</sup>. The room temperature spectrum shown in Figure 1b is a portion of this spectrum which we assigned to the third overtone of the N-H stretch. The peak at  $13114 \text{ cm}^{-1}$  disappeared with deuteration,  $\text{C}_4\text{D}_4\text{NH}$ , indicating its identity as a pure C-H stretch or combination band. Reilly<sup>28</sup> suggested that the peak at  $13209 \text{ cm}^{-1}$  was a hot band absorption based on the assignment of the hot band absorptions in the second N-H overtone spectrum<sup>35</sup>. At  $T_{140}$  (shown in Figure 1a), this peak at  $13209 \text{ cm}^{-1}$  increases in intensity relative to the other peaks in this region. A closer examination of these changes is made possible in Figure 2 where only the principal peak and the temperature dependent peak are shown at three temperatures,  $T_{140}$ ,  $T_{120}$ , and  $T_R$ . The intensity increase of the  $13209 \text{ cm}^{-1}$  peak with increasing temperature means that it is a hot band absorption. The change in the relative intensity from  $T_R$  to  $T_{120}$  and from  $T_R$  to  $T_{140}$  indicates that this absorption originated from a state lying at  $276 \text{ cm}^{-1}$  and  $405 \text{ cm}^{-1}$ , respectively, above the vibrationless level. The two different values obtained for  $\Delta E$  indicates that the increase of the band intensity is not described by a simple Boltzmann relation. This is probably due to the small changes in the band contour shape which result from changes in the rotational state populations with increasing temperature. As shown in Table 1, the bandwidth of the peaks increases about 20% going from room temperature to  $T_{140}$ . Since we do not resolve the rotational structure we cannot predict the magnitude of this effect.

Pyrrole has a strong infrared absorption<sup>41</sup> with a fundamental frequency of  $474 \text{ cm}^{-1}$  which we believe to be the active mode. This fundamental is the N-H wag of  $B_2$  symmetry labelled either  $v_{24}$  (ref. 42) or  $v_1$  (ref. 43) depending on the numbering convention. The calculated  $\Delta E$  values from our experiment agree with this low frequency mode, given our estimated experimental error of  $\pm 20\%$  (Table 1). The hot band lies  $100 \text{ cm}^{-1}$  to the red of the principal peak, making the anharmonic constant  $x_{ph}^0 = -25 \text{ cm}^{-1}$ . In the very early work of Zumwalt and Badger<sup>35</sup> on the second overtone spectrum of the N-H stretch in pyrrole, the two temperature dependent bands were shifted 74 and



146  $\text{cm}^{-1}$  to the red of the principal peak. This results in  $x_{\text{ph}}^0 = -25 \text{ cm}^{-1}$  similar to our results for the third overtone.

The peak to the blue of the principal peak in Figure 2 does not change its relative intensity and is therefore not a hot band absorption. We believe that the minor changes in the band contour for this peak relate to the expected changes in the rotational state population with temperature.

Figure 3 shows the temperature dependence of the  $3\nu_{\text{C-H}}$  in pyrrole. At room temperature this peak seems to be the overlap of two closely spaced transitions. The temperature effect is weak perhaps because of the small spectral shift and perhaps because this is not a hot band after all. The overall width does not change noticeably; however, the peak maximum shifts to the red by about 20  $\text{cm}^{-1}$  at high temperature which would result from an increase in hot band intensity. Here the spectral shift of the lower energy band is small, 41  $\text{cm}^{-1}$ , giving an anharmonic constant of  $x_{4\text{ph}}^0 = -10 \text{ cm}^{-1}$ . Compared to the  $\sim 20 \text{ cm}^{-1}$  value obtained in other cases, this may not be a hot band transition.

A temperature effect similar to the one we have identified in pyrrole seems to appear in the spectrum of propyne (Figure 5, reference 22). In part a. of that figure the temperature dependence of the (4-0) acetylenic C-H stretch region is shown. The band contour of the 12638  $\text{cm}^{-1}$  peak designated as W does contract at lower temperatures, as expected of a band that is predominantly broadened by rotational state population; however the overall band intensity decreases at lower temperature relative to the principal band. The decrease in intensity of this band is certainly the largest temperature effect observed in this spectrum. We believe that this absorption is a hot band absorption with a shift of 75  $\text{cm}^{-1}$ . This peak was also assigned as a hot band by Baylor et al.<sup>37</sup> in their work on the overtone spectroscopy of propyne. The anharmonic constant,  $x_{\text{ph}}^0$ , is about -19  $\text{cm}^{-1}$  which is in good agreement with the anharmonic constant reported<sup>37</sup> and similar to the values obtained in the present work in methyl isocyanide and isobutane (Table 1). In part b of the same figure, the spectrum of the (5-0) methyl C-H stretch was shown which is also of interest here. The two bands to the red of the principal peak were tentatively assigned to combinations of four quanta in the stretch plus other normal modes. These two bands show a large decrease in intensity with decreasing temperature and we believe there is hot band contribution to these peaks. The shift of the first peak estimated from the figure is  $\sim 110 \text{ cm}^{-1}$ , making the anharmonic constant,  $x_{\text{ph}}^0$ , about -22  $\text{cm}^{-1}$ .

### Methyl isocyanide

The photoacoustic spectrum of the fourth overtone of the C-H stretch in gaseous methyl isocyanide at room temperature was measured by Reddy and Berry<sup>44-46</sup>. Two broad, overlapping bands with peak maxima at 13765 and 13643  $\text{cm}^{-1}$  were obtained. Based on the normal mode analysis of the IR spectra, the authors tentatively assigned these bands as the fourth overtone C-H stretch  $5\nu_1$  and  $5\nu_5$  ( $\nu_1$  is the  $A_1$  symmetry mode at 2966  $\text{cm}^{-1}$  and  $\nu_5$  is the degenerate, E symmetry at 3014  $\text{cm}^{-1}$ ).

Typically overtone spectra are not assigned according to overtones of the normal mode fundamental frequencies, but to local modes which follow a Birge-Sponer relationship<sup>1</sup>. Vibrational

progressions are observed for each nonequivalent C-H oscillator within the molecule. Based on the observation of all 8 Raman bands predicted in the  $C_{3v}$  point group<sup>47</sup>, the CNC in methyl isocyanide is linear. This linearity<sup>48</sup> implies that all of the C-H bonds are equivalent, therefore the two observed peaks can not result from conformational inequivalence of the C-H bonds.

In Figure 4 we present our measured spectra at  $T_{\text{rt}}$  (a) and at  $T_{140}$  (b). The  $T_{\text{rt}}$  spectrum is similar to that of Reddy and Berry. It is clear that at high temperature the peak at lower energy gains intensity relative to the higher energy peak. The relative intensity of the lower energy peak to the main peak changed from 0.71 at  $T_{\text{rt}}$  to 0.93 at  $T_{140}$ . This would not be the case if the lower energy peak is  $5\nu_1$  as originally assigned. Although the high temperature spectrum is noisy, it is possible to say that no shift in the wavelengths occurred; however there was possibly a small increase in the width of the principal peaks. This implies that at room temperature the rotational linewidths are wide relative to the separation of the rotational features.

From the above, the increase in the intensity of the lower energy peak with temperature has to be a hot band vibrational effect. The CNC bending mode,  $\nu_8$ , in methyl isocyanide is assigned<sup>47,49</sup> to be  $263\text{ cm}^{-1}$ . We believe that the hot band absorption originated from this low frequency mode. The experimental  $\Delta E$  calculated from the change in the relative intensity of the peaks with temperature is  $208 \pm 40\text{ cm}^{-1}$ , which is the same as the bending frequency given the error of our experiment. The lower energy peak shifted  $100\text{ cm}^{-1}$  to the red relative to the main peak giving an anharmonicity,  $x_{\text{ph}}^0$ , of  $-20\text{ cm}^{-1}$ . This agrees with the other C-H overtone anharmonic constants in Table 1.

In light of our above discussion we want to reexamine the beautiful work on the second C-H stretch overtone absorption of benzene. Page et al.<sup>31</sup> showed that the principal peak at  $8827\text{ cm}^{-1}$  in the  $3\nu_{\text{C-H}}$  spectrum cooled to a width of  $10\text{ cm}^{-1}$  under supersonic cooling (Figure 2c in ref. 31a). Thus the band contour was dominated by inhomogeneous broadening which could be decreased by eliminating the population in higher rotational and vibrational states. The detection method used in this experiment selected only molecules in the ground vibrational state so no hot band absorptions would be observed even though the spectral scan covered the entire  $200\text{ cm}^{-1}$  range around the principal peak. By selecting different groups of  $J$  states within the ground states rotational manifold, these workers believed they saw evidence for four different vibrational transitions within a  $72\text{ cm}^{-1}$  range. The same overtone was reexamined by Bassi et al.<sup>32</sup> using a simple optothermal absorption detection with a supersonic expansion of benzene. Their measured spectrum is shown in Figure 5. It is well known that the vibrations of benzene do not cool completely in a supersonic expansion. Snively et al.<sup>50</sup> found the vibrational temperature to be 150 K in a supersonic expansion of benzene while the rotational temperature was as low as 80 K. In Bassi's experiment the hot bands should be observed. However, they did not interpret any of the seven observed vibrational transitions as hot bands. From comparison of the spectra obtained in the above two experiments, we believe the peak at  $8770\text{ cm}^{-1}$  shown in Figure 5 is a hot band. Page identified three vibrational transitions at 8086, 8854, and  $8878\text{ cm}^{-1}$  in addition to the strong principal peak at  $8827\text{ cm}^{-1}$ . Bassi confirmed three of these transitions but did not observe the peak at  $8878\text{ cm}^{-1}$ . Four vibrational transitions around  $8770\text{ cm}^{-1}$  observed by Bassi were not detected by Page. The small decrease in the relative intensity of the

peak at  $8870\text{ cm}^{-1}$  in the molecular beam relative to the room temperature photoacoustic spectrum (Figure 5), is expected if the vibrational temperature in the beam was as high as 150 K due to slow vibrational cooling. This peak shifted from the principal peak by  $57\text{ cm}^{-1}$ , making the anharmonic constant,  $x_{\text{ph}}^0$ , about  $-19\text{ cm}^{-1}$  in good agreement with our other results (Table 1).

These spectroscopic results have interesting consequences on the interpretation of our vibrational overtone activation of the isomerization of methyl isocyanide to acetonitrile<sup>51</sup>. We measured the specific rate coefficient for this reaction at four different wavelengths across the band contour of the  $5\nu_{\text{C-H}}$  transition. The rate coefficient increased monotonically with increasing photolysis energy. These measured rates corresponded exactly to the calculated specific rate coefficients calculated in RRKM theory. Four photolysis wavenumbers at the  $5\nu_{\text{C-H}}$  were used:  $13763\text{ cm}^{-1}$  at the peak maximum, two wavenumbers to the red of the maximum,  $13605$  and  $13738\text{ cm}^{-1}$ , and  $13788\text{ cm}^{-1}$  to the blue. In the present work the peak at  $13605\text{ cm}^{-1}$  is assigned as a hot band, most likely based on the CNC bend. If this assignment is true, molecules excited at  $13605\text{ cm}^{-1}$  possess more internal energy than those photolyzed at higher wavenumbers. Using the bending energy plus the photon energy, molecules photolyzed at  $13605\text{ cm}^{-1}$  would possess about  $100\text{ cm}^{-1}$  more internal energy than those photolyzed at the peak maximum,  $13763\text{ cm}^{-1}$ . Given the experimental error in our rate coefficients we would have been able to measure this difference in the rates and should have observed a nonmonotonic increase with increasing photolysis energy. An explanation of our kinetic results could be that we see hot band temperature dependence in the red side of the  $5\nu_{\text{C-H}}$  transition but it is possible that there are other vibrational transitions contributing to the overall contour of the red peak. This is similar to the observations in benzene where we believe that some of Bassi's remaining seven peaks are hot bands but some are combination bands. Perhaps at the one photolysis wavenumber chosen on the red side of the  $5\nu_{\text{C-H}}$ , we were photolyzing a combination band rather than a hot band transition. This would explain our monotonic increase in the specific rate coefficient with increasing energy.

### Acetonitrile

The fourth overtone spectrum of acetonitrile at  $T_{\text{R}}$  and at  $T_{140}$  is shown in Figure 6. The spectrum is similar to the one obtained by Reddy and Berry<sup>46</sup>. However, compared to methyl isocyanide only one peak, centered at  $13718\text{ cm}^{-1}$ , is observed in the same spectral range. A second relatively weak absorption appeared at  $\sim 13550\text{ cm}^{-1}$ , which did not change with temperature. The band contour of the main peak reveals some rotational structure, indicating that the linewidth is on average narrower than the line spacing. Accordingly, the high temperature bandwidth increased by about  $20\text{ cm}^{-1}$  from that of the room temperature spectrum. This increase in width does occur mostly on the red side of the rotational contour but it is impossible for us to tell whether this results simply from the rotational state population increase or an increase in the intensity of a hot band. The CCN bending mode frequency,  $\nu_8$ , in acetonitrile<sup>52</sup> occurs at  $364\text{ cm}^{-1}$ , which is  $\sim 100\text{ cm}^{-1}$  higher than the CNC bend in methyl isocyanide. This higher bending frequency is one of the reasons why the hot band transition is not observed in acetonitrile.

### Cyclohexane

The overtone spectrum of cyclohexane is characterized by two vibrational progressions of the axial and equatorial C-H stretches<sup>53</sup>. These oscillators possess different fundamental frequencies due to their nonequivalent positions within the molecule. The  $6\nu_{\text{C-H}}$  overtone transition of cyclohexane should display two closely overlapping peaks similar to methyl isocyanide, however in this case, these peaks should have no temperature dependent intensity changes relative to one another. Figure 7 shows that the relative intensity of the peaks did not change with temperature (Table 1) confirming our expectations.

### Isobutane

The  $6\nu_{\text{C-H}}$  overtone absorption spectrum of isobutane at 140, 120 and 25 C is shown in Figure 8. The peak at  $15710\text{ cm}^{-1}$  increases in intensity relative to the main peak at  $15835\text{ cm}^{-1}$  with increasing temperature. We believe that the  $15710\text{ cm}^{-1}$  peak is a hot band.

The lowest frequency fundamental<sup>54</sup>,  $\nu_8$ , occurs at  $426\text{ cm}^{-1}$ . The calculated  $\Delta E$  from the change in the relative intensities going from room temperature to 120 and 140 C are 190 and  $410\text{ cm}^{-1}$ , respectively. Again, the two different  $\Delta E$  values indicates nonBoltzmann growth of the intensity. There are two possible explanation for this. The bandwidths at high temperature do increase (Table 1) indicating that changes in the rotational state populations have altered the band contour shape. When this is the case our simple fitting procedure, which does not take into account any band contour shape changes, is less useful and does not yield actual experimental intensity changes. The second possibility is that other vibrational transitions, which are not affected by temperature, occur at wavelengths close to the hot band. The hot band shift is  $120\text{ cm}^{-1}$ , giving  $x_{\text{ph}}^0 = -20\text{ cm}^{-1}$  for the anharmonicity.

Surprisingly, no temperature dependence was observed in the  $5\nu_{\text{C-H}}$  overtone spectrum of isobutane at 189 K presented by Crofton et al.<sup>22</sup>. The two intense peaks were tentatively assigned to the methyl C-H oscillators while the third weak peak at  $\sim 13240\text{ cm}^{-1}$  was assigned to the remaining C-H. In light of the temperature dependence described for the  $6\nu_{\text{C-H}}$  we repeated the experiment on  $5\nu_{\text{C-H}}$  and found no temperature dependence (Figure 9). We had expected isobutane to have two unequivalent C-H oscillators - the methyl C-H's and the single C-H leaving the peak at  $13358\text{ cm}^{-1}$  to be a hot band.

A comparison of the room temperature bandwidths for both overtones shows that the bandwidth for the lower overtone is larger. This may result from overlapping vibrational transitions. If this is the case, higher temperatures are needed to observe the increase in the relative intensity of the hot band peaks. Although we have not shown that this is a hot band, the peak at  $13358\text{ cm}^{-1}$  lies  $100\text{ cm}^{-1}$  to the red of the principal peak, making the anharmonicity,  $x_{\text{ph}}^0 = -20\text{ cm}^{-1}$ , in good agreement with the other observed values.

### Conclusion

Many room temperature overtone spectra exhibit two or more overlapping peaks where only the main band is assigned. Some of these absorptions arise from unequivalent C-H oscillators within the molecule but some exhibit temperature dependence indicating their identity as hot bands.

Local mode spectra are characterized by large diagonal anharmonicities. These are typically -50 to 60  $\text{cm}^{-1}$  for C-H oscillators. Usually it is thought that anharmonicities for hot bands will be small, on the order of a few wavenumbers. We have documented four cases where hot band absorptions are unexpectedly intense in the visible vibrational spectrum. The anharmonicities for these absorptions are large ranging from -20 to -25  $\text{cm}^{-1}$ . Even with low resolution spectra these hot bands are easy to identify because the spectral shift is the product of the anharmonicity and the quantum numbers for the upper states. The spectral shifts are so large that it is probably the case that these features have been assigned in the past to combination bands or possibly peaks due to unequivalent oscillators.

We believe that major contributions to overtone spectra come from hot band absorptions with large off-diagonal anharmonicities. These hot band transitions contrive in such a way to overlap the principal local mode absorption thus broadening the overall band contributing to its psuedo-Lorentzian lineshape.

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## Figure Captions:

Figure 1. The  $4\nu_{N-H}$  overtone photoacoustic absorption spectrum of pyrrole: (a) at 140 C and (b) at room temperature.

Figure 2. The main and the hot band peaks of the  $4\nu_{N-H}$  overtone photoacoustic absorption spectrum of pyrrole showing the relative intensity and band contour changes : (a) at 140 C, (b) at 120 C and (c) at room temperature.

Figure 3. The  $4\nu_{C-H}$  overtone photoacoustic absorption spectrum of pyrrole: (a) at 140 C and (b) at room temperature.

Figure 4. The  $5\nu_{C-H}$  overtone photoacoustic absorption spectrum of methyl isocyanide: (a) at 140 C and (b) at room temperature.

Figure 5. The room temperature photoacoustic spectrum (open circles) and the molecular beam optothermal spectrum (vertical bars) of the  $3\nu_{C-H}$  overtone absorption of benzene obtained by Bassi et al., taken from ref. 29.

Figure 6. The  $5\nu_{C-H}$  overtone photoacoustic absorption spectrum of acetonitrile: (a) at 140 C and (b) at room temperature.

Figure 7. The  $6\nu_{C-H}$  overtone photoacoustic absorption spectrum of cyclohexane: (a) at 140 C and (b) at room temperature.

Figure 8. The  $6\nu_{C-H}$  overtone photoacoustic absorption spectrum of isobutane: (a) at 140 C, (b) at 120 C and (c) at room temperature.

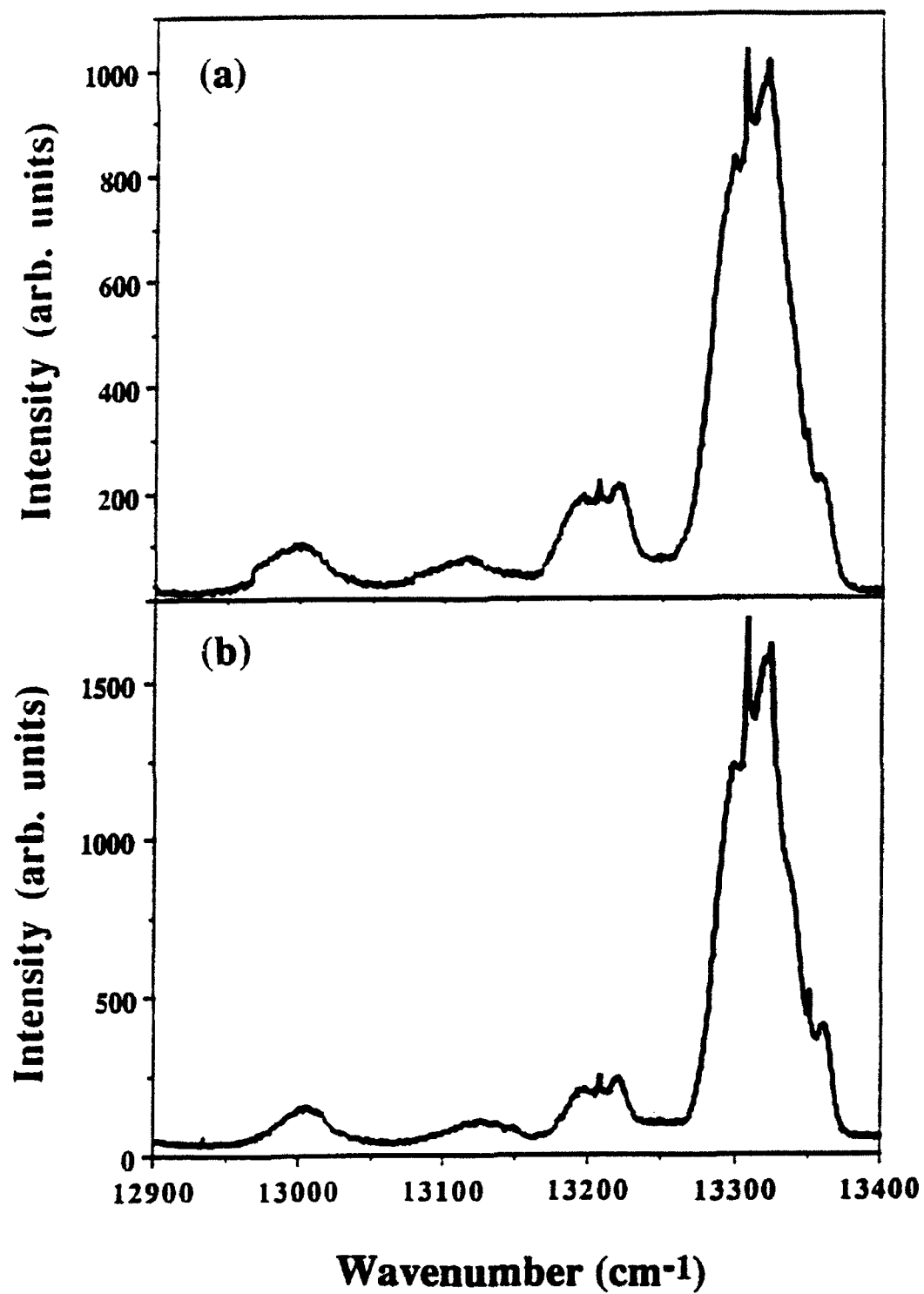
Figure 9. The  $5\nu_{C-H}$  overtone photoacoustic absorption spectrum of isobutane: (a) at 140 C and (b) at room temperature.



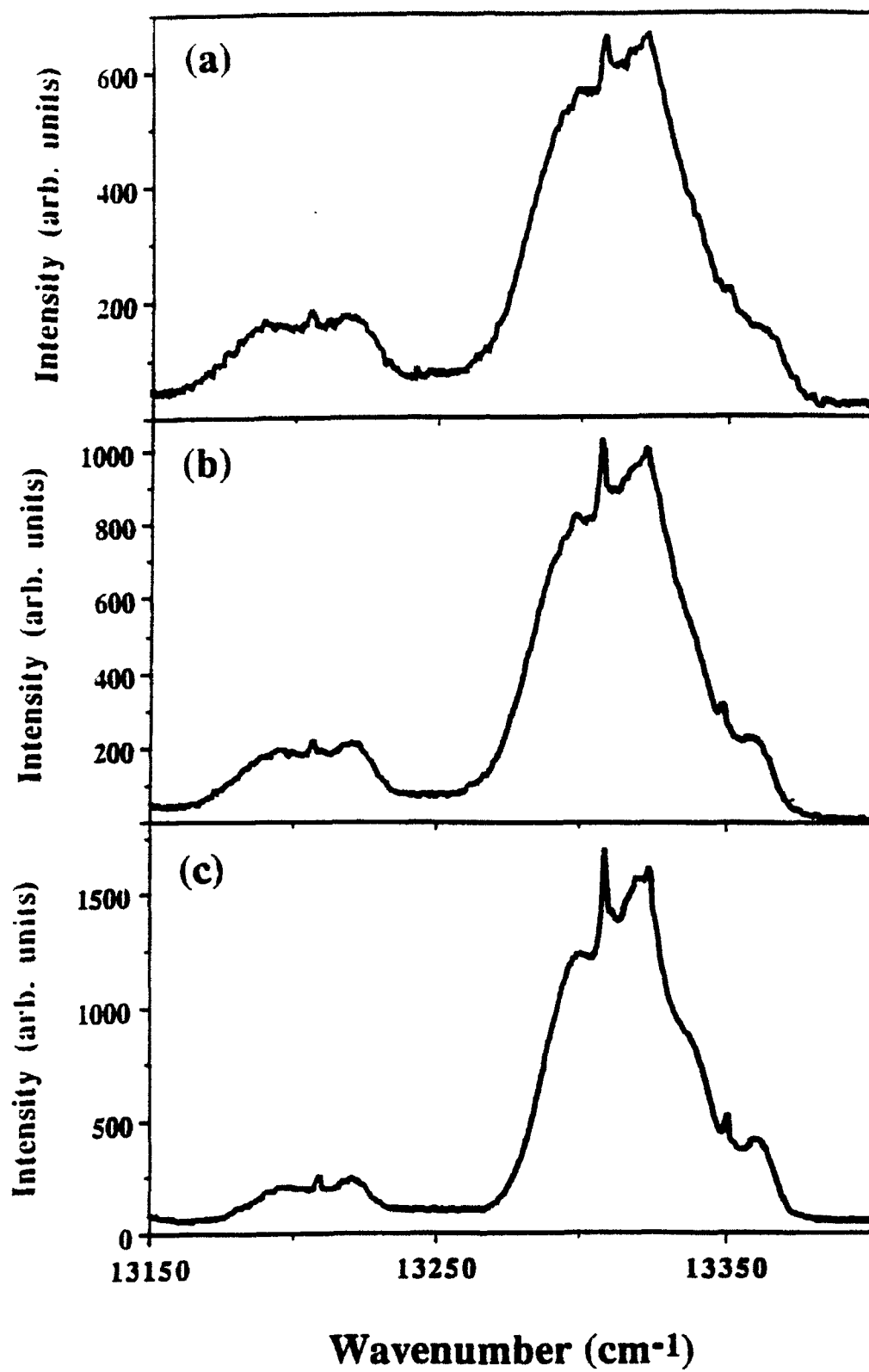
TABLE I. Band frequencies, widths, relative intensities and anharmonicities for the observed spectra.

Sample	Overtone Transition	Temp. (C)	Band Center $\nu_1$ (cm <sup>-1</sup> )	Band Center $\nu_2$ (cm <sup>-1</sup> )	FWHM (1) (cm <sup>-1</sup> )	FWHM (2) (cm <sup>-1</sup> )	Relativ Int. $I_2 / I_1$	$\Delta E$ Calculated (cm <sup>-1</sup> )	Bending Freq. (cm <sup>-1</sup> )	Anharmonic Constant (cm <sup>-1</sup> )
Methyl isocyanide	5V <sub>C-H</sub>	25±2	13760±10	13660±10	95±10	100±10	0.71±0.07	-	-	-20±2
		140±5	13760±10	13660±10	100±10	150±10	0.93±0.09	208±40	263 <sup>a</sup>	-
Aceto- nitrile	5V <sub>C-H</sub>	25±2	13718±10	-	93±10	-	-	-	-	-
		140±5	13720±10	-	107±10	-	-	-	364 <sup>b</sup>	-
Pyrrole	4V <sub>N-H</sub>	25±2	13309±10	13209±10	45±10	38±10	0.12±0.01	-	-	-25±2
		120±5	13307±10	13207±10	52±10	45±10	0.17±0.02	276±80	-	-25±2
		140±5	13307±10	13209±10	57±10	50±10	0.21±0.02	405±80	474 <sup>c</sup>	-25±2
	4V <sub>C-H</sub>	25±2	11850±10	11800±10	-	-	-	-	-	-13±2
		140±5	11831±10	11800±10	-	-	-	-	-	-8±2
		-	-	-	-	-	-	-	-	-
Isobutane	6V <sub>C-H</sub>	25±2	15835±10	15710±10	65±10	98±10	0.38±0.04	-	-	-21±2
		120±5	15833±10	15714±10	70±10	110±10	0.48±0.05	198±40	-	-20±2
		140±5	15844±10	15710±10	100±10	120±10	0.66±0.07	418±80	426 <sup>d</sup>	-22±2
	5V <sub>C-H</sub>	25±2	13458±10	13358±10	106±10	106±10	0.52±0.05	-	-	-20±2
		140±5	13458±10	13358±10	128±10	106±10	0.52±0.05	-	-	-20±2
		-	-	-	-	-	-	-	-	-
Cyclo- hexane	5V <sub>C-H</sub>	25±2	15585±10	15368±10	150±10	200±10	0.80±0.08	-	-	-
		140±5	15585±10	15368±10	164±10	200±10	0.80±0.08	-	-	-

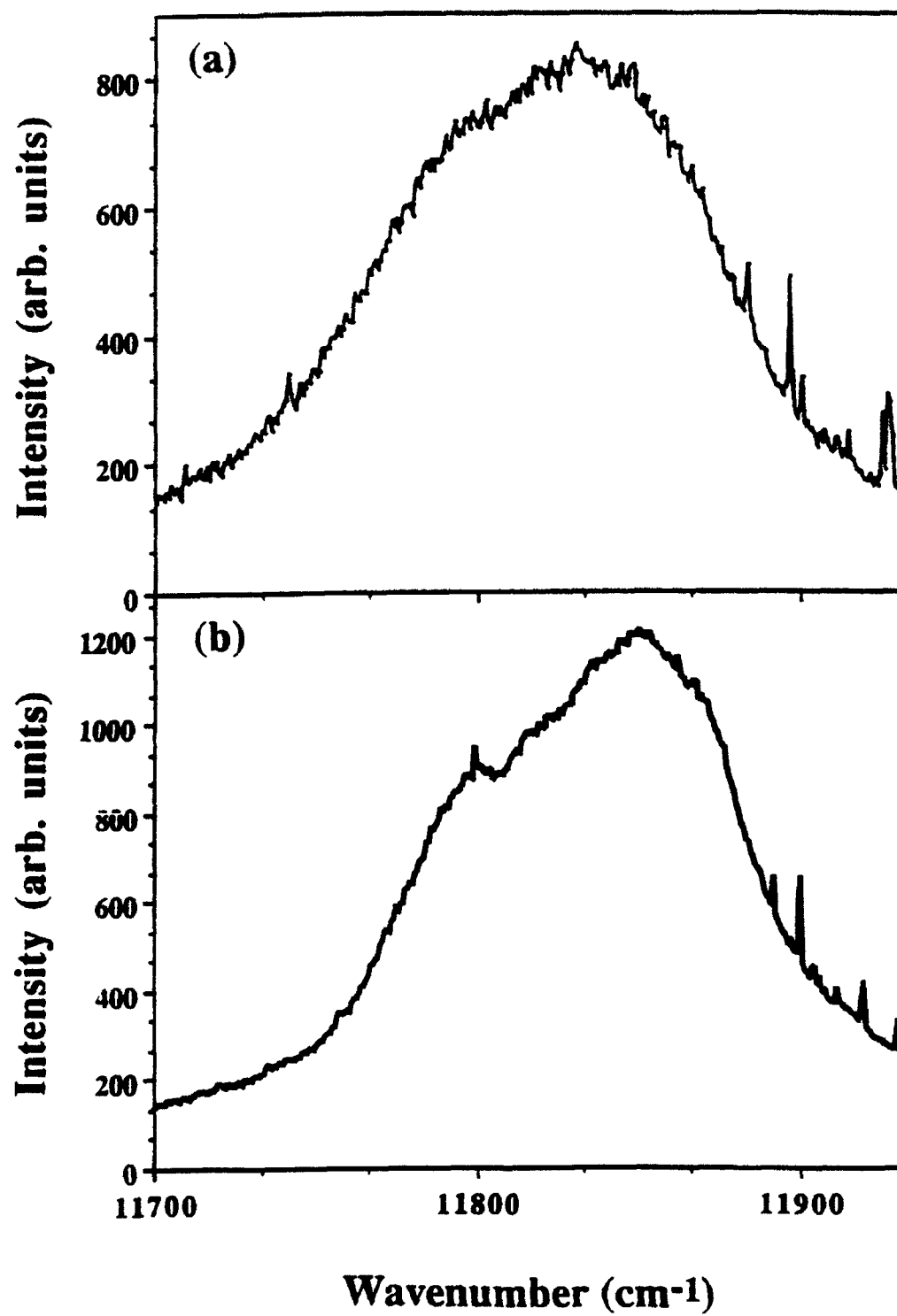
(a) ref. 47, 49; (b) ref. 52; (c) ref. 40; (d) ref. 54



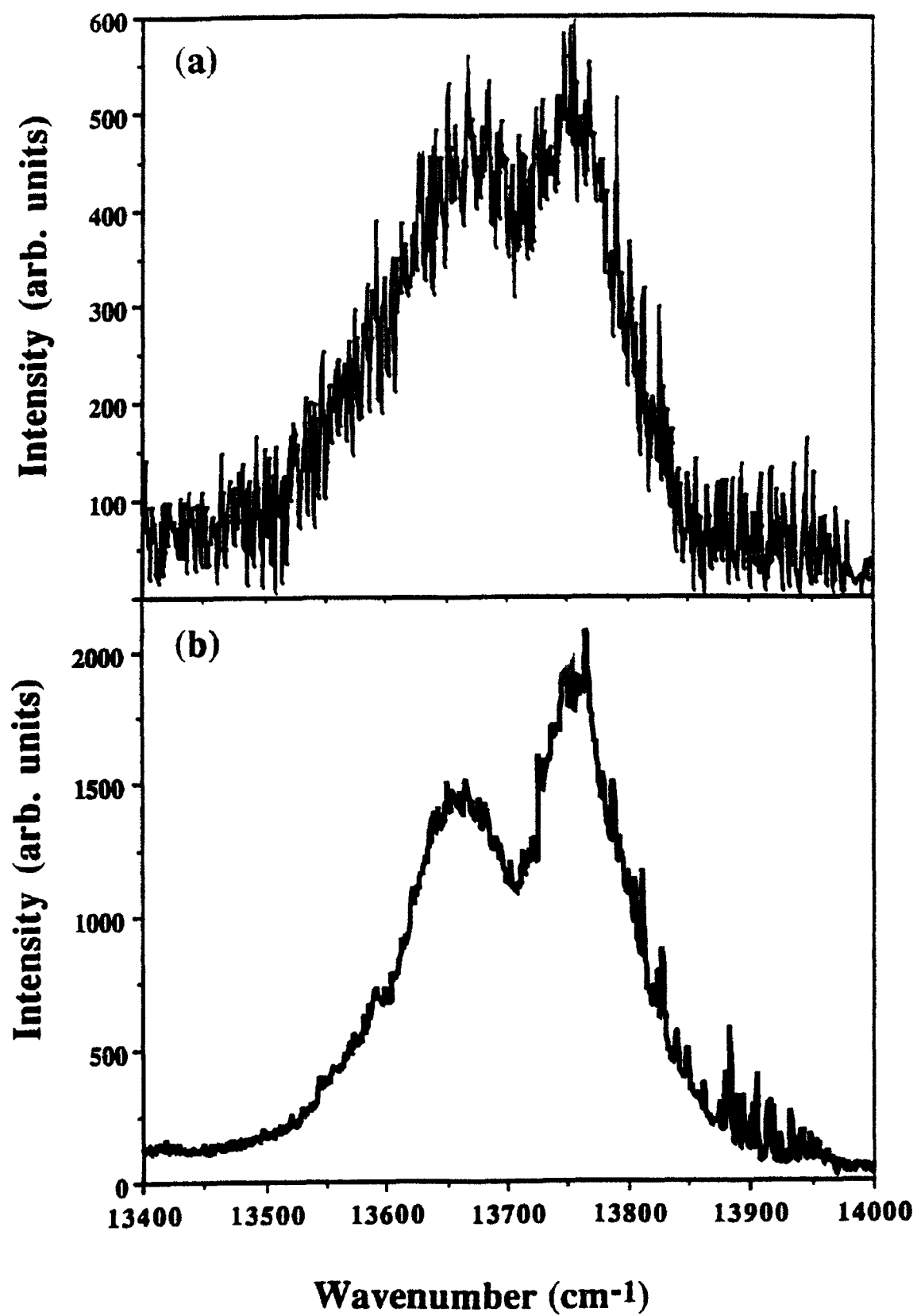
**Figure 1**



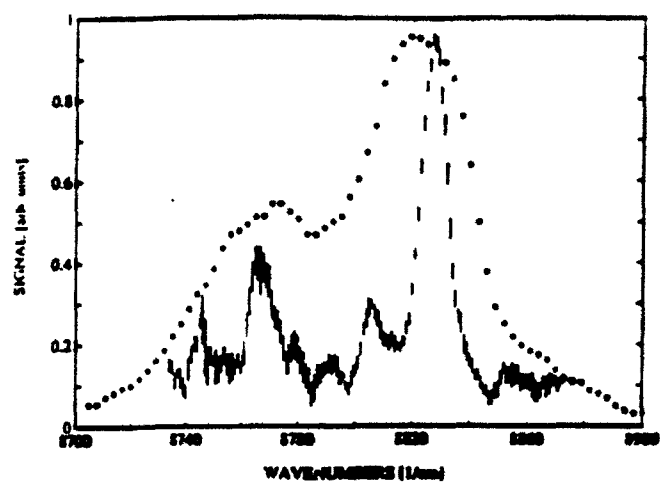
**Figure 2**



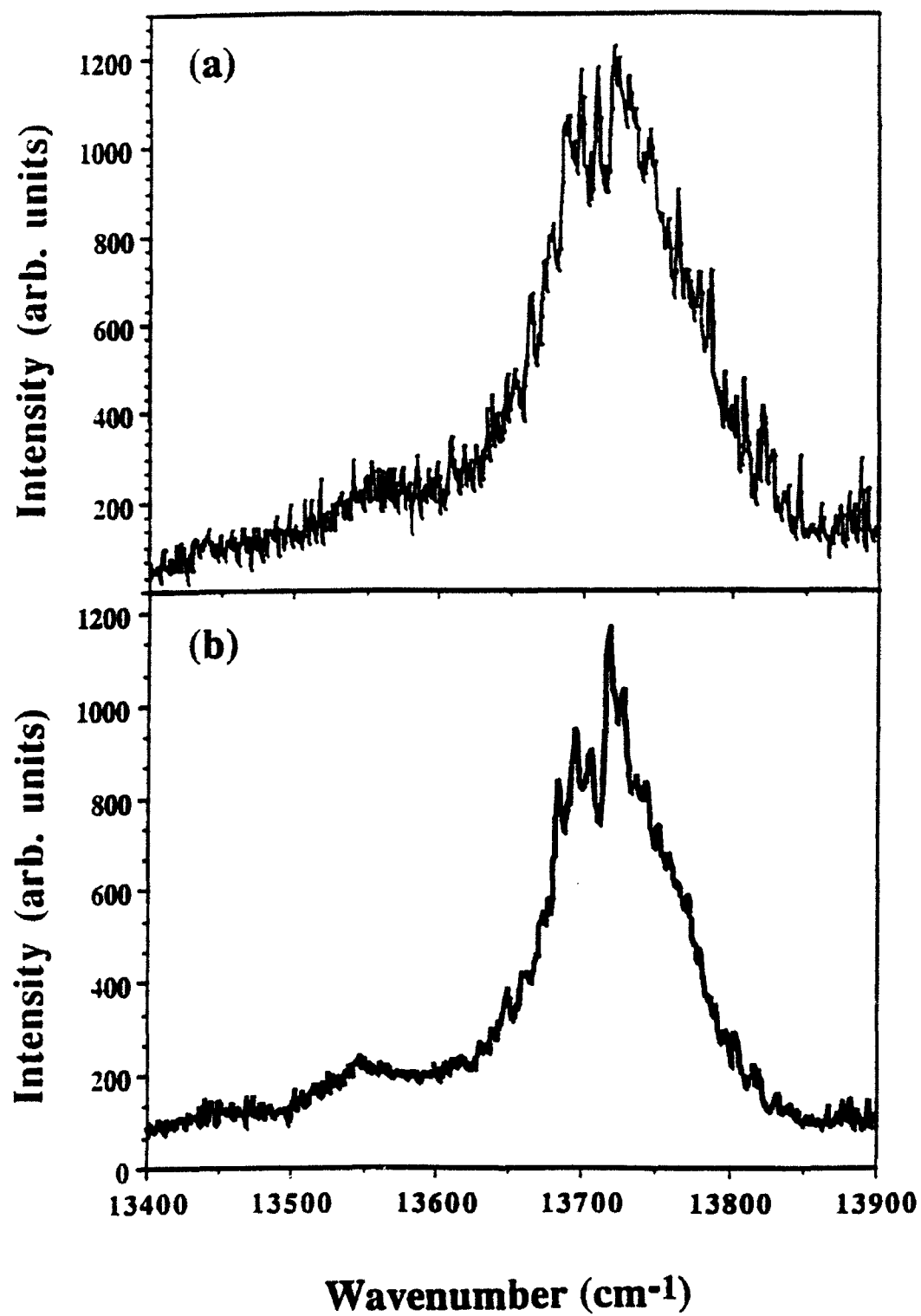
**Figure 3**



**Figure 4**



**Figure 5**



**Figure 6**

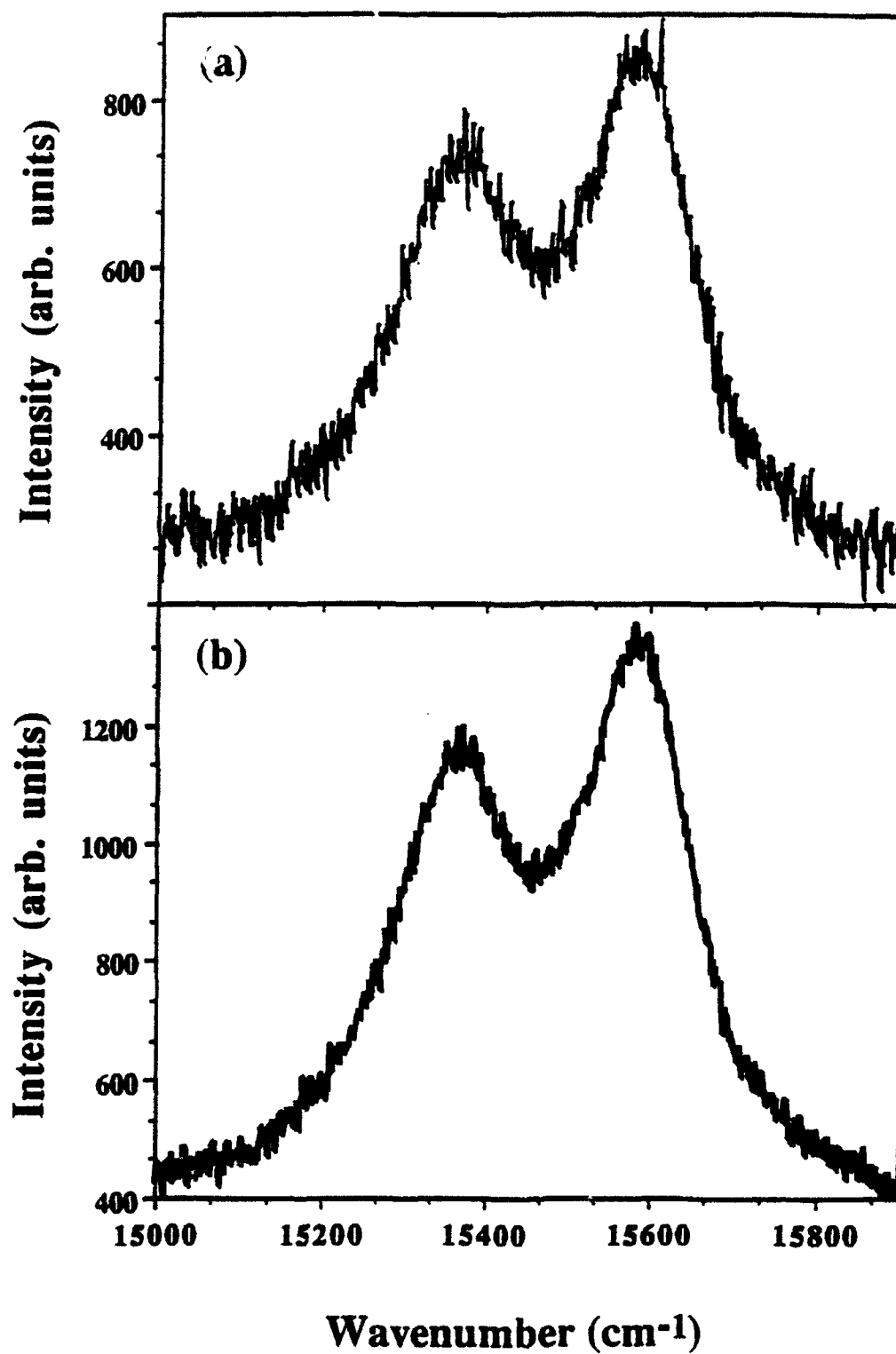
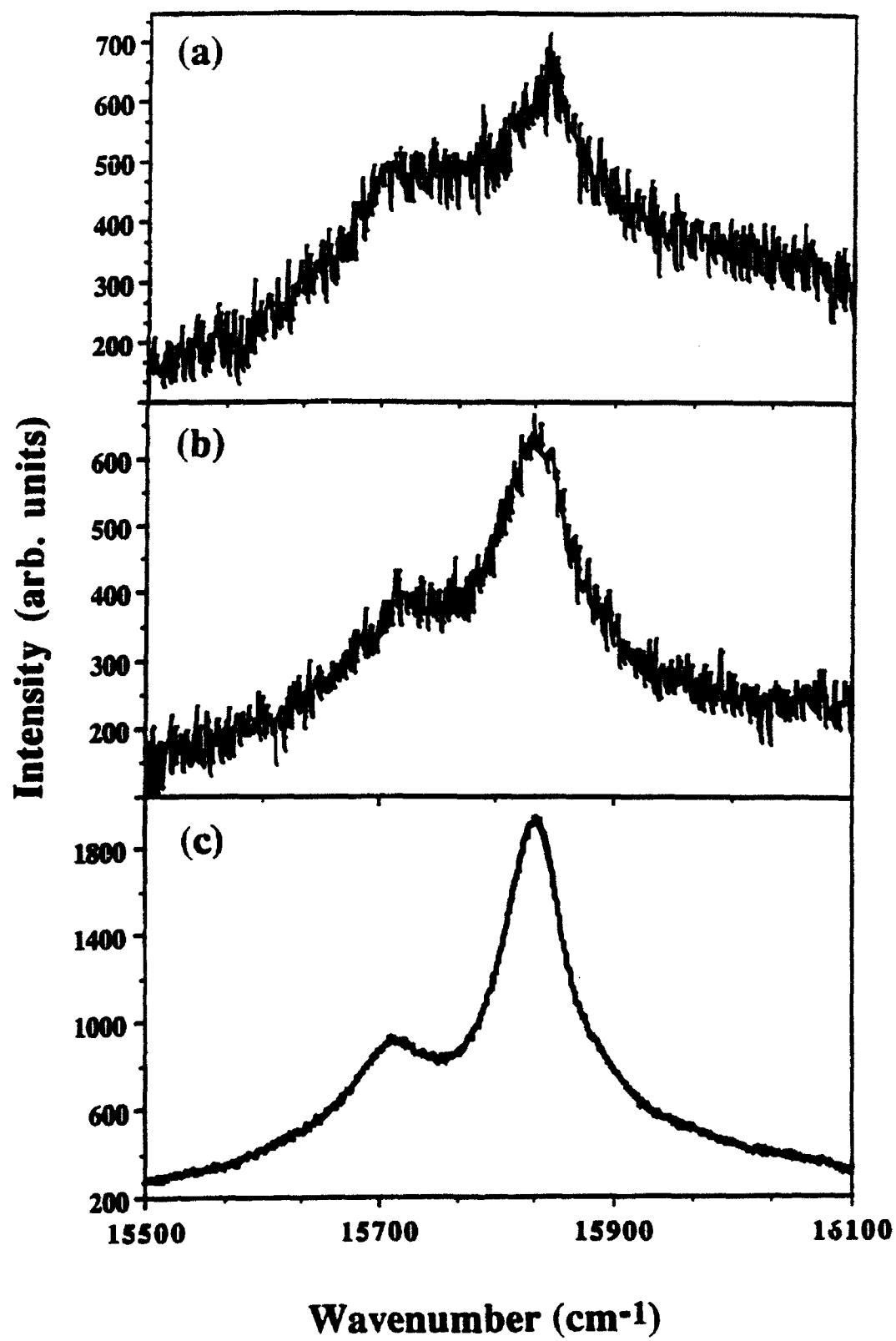
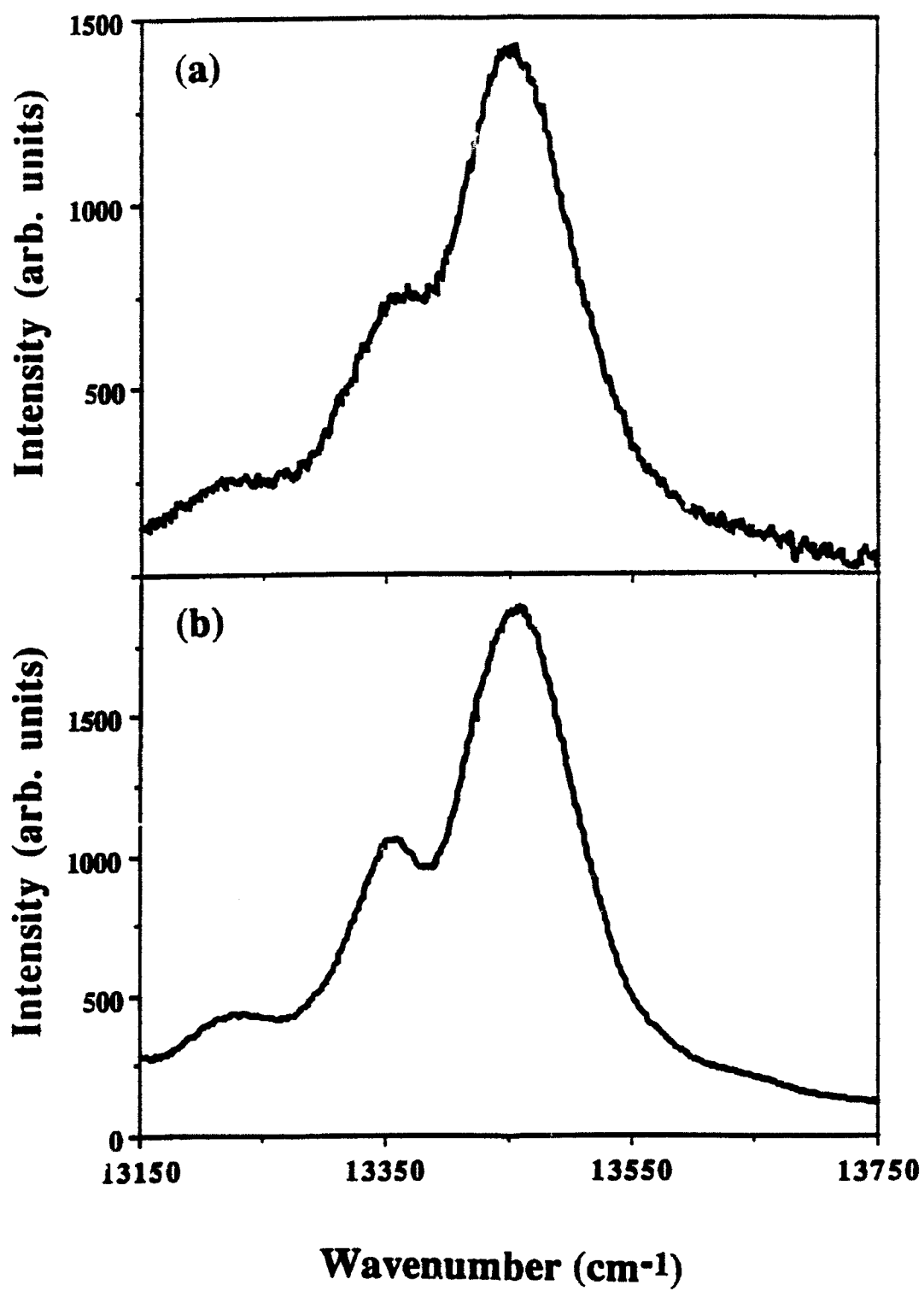


Figure 7





**Figure 8**



**Figure 9**